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पेट्रोलियम और इसके उत्पादों की परीक्षण पद्धतियाँ

[पी : 79]

पेट्रोलियम उत्पादों में अनुरेखण तत्वों को ज्ञात करना — वेनेडियम

(पहला पुनरीक्षण)

Indian Standard

METHODS OF TEST FOR PETROLEUM AND ITS PRODUCTS

[P : 79]

DETERMINATION OF TRACE ELEMENT IN PETROLEUM PRODUCTS — VANADIUM

(First Revision)

UDC 665·6/·7 : 543 [546·881]

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NEW DELHI 110002

November 1992 **Price Group 3**

Methods of Test for Petroleum, Petroleum Products and Lubricants Sectional Committee, PCD 1

FOREWORD

This Indian Standard [P : 79] (First Revision) was adopted by the Bureau of Indian Standards, after the draft finalized by the Methods of Test for Petroleum, Petroleum Products and Lubricants Sectional Committee had been approved by the Petroleum, Coal and Related Products Division Council.

In reporting the results of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'.

Indian Standard

METHODS OF TEST FOR PETROLEUM AND ITS PRODUCTS
[P : 79]
DETERMINATION OF TRACE ELEMENT IN PETROLEUM PRODUCTS — VANADIUM

(First Revision)

Adapted with permission from ASTM D 1548-83

1 SCOPE

1.1 This standard describes a procedure for the determination of vanadium in the range of up to and including 350 ppm in heavy petroleum products, such as residual fuel oils. Other elements commonly found in Navy special fuel oils do not interfere.

1.2 This standard may involve hazardous materials, operations and equipments. This standard does not purport to address all the safety problem associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2 REFERENCES

The following Indian Standards are necessary adjuncts to this standard:

IS No.	*Title*
264 : 1976	Nitric acid (*second revision*)
266 : 1977	Sulphuric acid (*second revision*)

3 OUTLINE OF THE METHOD

The fuel oil is treated with concentrated sulphuric acid; the mixture reduced to acid-free coke; and then dry ashed at 525 ± 25°C. Mixed acids are added to the inorganic ash and the residue reduced to sulphuric acid fumes. The residue is dissolved in water, phosphoric acid and sodium tungstate are added, and vanadium is determined by measuring the absorbance of its phosphotungstovanadic acid complex at 436 nm. The vanadium concentration is obtained from the absorbance by means of a previously prepared calibration curve.

NOTE — The temperature for ashing should not exceed 550°C, otherwise the vanadium compounds will be lost resulting in lower vanadium content in the sample.

4 SIGNIFICANCE AND USE

Vanadium in fuels may form low melting compounds that are severely corrosive to metal parts.

5 APPARATUS

5.1 Electric Muffle Furnace

5.1.1 Capable of operating between 150 and 550°C, and of maintaining a temperature of 525 ± 25°C.

5.2 Spectrophotometer or Photoelectric Photometer

5.2.1 Equipped with an interference-type filter capable of isolating a relatively narrow band of 10 nm in the region of 436 nm.

NOTE — The wavelength measurement is critical because at lower wavelength serious interference with iron occurs. A spectrophotometer is preferred; but if this is not available, a colorimeter fitted with an interference type filter capable of isolating a 10 nm band width at 436 nm may be used.

6 REAGENTS

The following reagents shall be used for this test (*see also* Annex A).

6.1 Concentrated Nitric Acid — relative density 1·42 (*see* IS 264 : 1976).

CAUTION: DANGER — POISON. Causes severe burns. Harmful or fatal if swallowed or inhaled.

6.2 Phosphoric Acid — (1:2). Mix 1 volume of concentrated phosphoric acid (H_3PO_4, 85 per cent) with 2 volumes of water.

CAUTION: *See* CAUTION under **6.1**.

6.3 Standard Potassium Permanganate Solution — 0·1 N. Dissolve 3·2 g of potassium permanganate ($KMnO_4$) in one litre of water. Let it stand in the dark for 2 weeks and filter without washing, through a Gooch crucible or a fritted glass crucible of fine porosity, avoiding contact with rubber or other organic material. Store in a dark-coloured glass-stoppered bottle. Standardize against a standard solution of sodium oxalate.

CAUTION: DANGER — CORROSIVE. Can cause severe burns or blindness. Evolution of heat produces a violet reaction or eruption upon too rapid mixture with water.

6.4 Sodium Tungstate Solution — 185 g/l. Dissolve 18·5 g of sodium tungstate dihydrate ($Na_2WO_4 . 2H_2O$) in hot water, filter, and dilute to 100 ml with cold water.

6.5 Concentrated Sulphuric Acid — relative density 1·84 (*see* IS 266 : 1977).

CAUTION — *See* CAUTION under **6.1**.

6.6 Sulphuric Acid — (1:1). Carefully add, with stirring, 1 volume of sulphuric acid (H_2SO_4) (relative density 1·84) to 1 volume of water.

6.7 Standard Vanadium Solution — (1 ml = 0·5 mg V). Place 0·446 3 g of vanadium pentoxide (V_2O_5) in a 400-ml beaker and treat it as described in **9.6** and **9.7**, except for adding 4 ml of sulphuric acid rather than the 2 ml specified in **9.6**. Wash carefully with distilled water into a volumetric flask and dilute to 500 ml. One millilitre of this solution contains 0·5 mg of vanadium.

NOTE — To determine the purity of vanadium pentoxide, add a 50 ml aliquot of the solution as prepared in 6.7 to a 500-ml Erlenmeyer flask. Add 150 ml of water and 4 ml of concentrated sulphuric acid and heat to boiling. Pass sulphur dioxide (SO_2) through the solution for 10 minutes. Remove the dissolved sulphur dioxide by passing carbon dioxide (CO_2) through the boiling solution for 10 minutes. Test for complete removal of sulphur dioxide by passing the exit carbon dioxide through a glass tube into the bottom of a 50-ml beaker containing 30 ml of water, 1 ml of sulphuric acid (1:1) and two drops of 0·1 N potassium permanganate. Cool the vanadium solution to 60 to 80°C and titrate it with standard potassium permanganate solution. If the vanadium pentoxide is less than 99 percent pure, weigh out a correspondingly larger amount than the 0·446 3 g as specified under 6.7.

Alternatively, standard vanadium solution (1 ml = 0·5 mg V) may also be prepared by dissolving 0·574 0 g of ammonium metavanadate in 65 ml of concentrated nitric acid and diluting with water to 500 ml in a volumetric flask.

CAUTION: DANGER — POISON. May be fatal if swallowed or absorbed through skin.

6.8 Standard Vanadium Solution (1 ml = 0·05 mg V) — Pipette 10 ml of the stock vanadium solution (1 ml = 0·5 mg V) into a 100 ml volumetric flask and dilute to volume with water.

7 SAMPLING

7.1 Obtain a representative sample in a clear and clean glass bottle, but do not fill the bottle more than about two-thirds full. If the sample is viscous, warm it until it is readily mixed. Just prior to weighing out the sample, stir up any material that has settled to the bottom and shake the bottle for 3 minutes.

7.2 Sample Size

7.2.1 The required sample size depends on the amount of vanadium present, the length of the light path of the absorbance cell, and the final sample dilution. For a 1-cm cell and a final sample dilution of 50 ml, the optimum sample size is one equivalent to 0·5 mg of vanadium, though samples equivalent to 0·2 to 0·8 mg are satisfactory. Calculate the approximate optimum sample size as follows:

$$\text{Sample size} = \frac{F}{C}$$

where

F = sample factor given in Table 1, and

C = expected vanadium concentration in parts per million.

NOTE — With samples containing less than about 10 ppm vanadium, it is advisable to employ absorption cells having up to 5 cm light path, and a final dilution volume of 25 ml rather than 50 ml to avoid ashing excessively large quantities of oil.

Table 1 Sample Factor

Absorbance Cell	Final Sample Dilution	Sample Factor, *F*
(1)	(2)	(3)
cm	ml	
1	50	500
1	25	250
2	50	250
2	25	125
5	50	100
5	25	50

8 CALIBRATION

8.1 When using 1-cm absorption cells, pipette into four 100-ml beakers, 0, 5·0, 10·0 and 20·0 ml aliquots of vanadium solution (1 ml = 0·05 mg V). If 2 or 5 cm absorption cells are employed, proportionately smaller amounts of the vanadium solution are required. Dilute to a total volume of about 30 ml with water and develop the colour as described in **9.9**.

8.2 Prepare a calibration curve by plotting the absorbance or transmittance against milligrams of vanadium in 50 ml of solution.

9 PROCEDURE

9.1 Weigh into a borosilicate glass beaker the appropriate size sample, as given in **7.2**, with an accuracy of at least 1 part per 100 parts of sample. Add 1 ml of concentrated sulphuric acid for each gram of sample. The size of the beaker should be at least three to four times the combined volume of acid and sample, and not more than 100 g of sample should be treated with the acid at one time. For samples low in vanadium content, which may require repeating the sulphonation step, obtain the sample mass by difference between the initial and final mass of the sample bottle.

9.2 Prepare a reagent blank, using the same amount of sulphuric acid as for the sample, and carry out the various steps given in the procedure as for the sample.

9.3 Place the beaker containing acid and sample on a high temperature hot-plate in a well ventilated hood and heat rapidly while stirring with a glass-rod (*see* CAUTION). When boiling or frothing starts, stir the sample mixture vigorously. Control the frothing by alternatively removing the beaker from the hot-plate and again placing it on the hot-plate. The heating and stirring of the acid mixture affects its sludging characteristics which depend on the nature of the sample. Give constant attention to each sample mixture until all danger of spattering and foaming is past.

> CAUTION: Hot fuming concentrated sulphuric acid is a very strong oxidizing acid. The analyst should wear rubber gloves and suitable face protection in case of spattering of the sulphuric acid.

9.4 As the foaming ceases and the acid sludge begins to thicken, place the acid mixture on a hot-plate at a high temperature and stir intermittently until the dense white fumes of sulphur dioxide have been emitted. Ignite with a burner, whatever hydrocarbon vapours are present will burn, and continue heating until a dry coke is obtained and sulphur oxide fumes are eliminated. Stirring the mixture occasionally hastens the reduction of the sample to a dry coke.

9.5 Place the beaker containing the dry coke into a muffle furnace at 150°C, increase the temperature to 525°C, and introduce a slow flow of air or oxygen into the furnace to aid in reducing the coke to inorganic ash. This usually requires several hours and is conveniently done by leaving the beaker in the furnace overnight.

> NOTE — The temperature-indicating device for the furnace should be checked for accuracy and the temperature never allowed to rise above 550°C. During the initial ignition period, adjust the muffle door so that too great an air flow into the muffle will not cause the ash to be blown from the beaker or to be lost because of too rapid burning of the carbonaceous material. Particular care should be taken to avoid contamination of the sample with particles from the roof, walls, and door of the furnace.

9.6 Colour Development

9.6.1 To the cooled beaker containing inorganic sulphated ash, add the following acids in the order listed: 2 ml of nitric acid and 2 ml of concentrated sulphuric acid. Heat carefully on a hot-plate until most of the nitric acid is evaporated and white fumes just begin to appear. At this point remove from the hot-plate.

> NOTE — Heating at the temperature of fuming sulphuric acid in the absence of nitric acid may cause low results due to reduction of pentavalent vanadium.

9.7 Wash the sides of the beaker cautiously with about 15 ml of water, heat to boiling, and cool. Neutralize by adding sodium hydroxide solution dropwise until the *p*H is between 6 and 10 as shown by placing a fraction of a drop on wide range *p*H paper. Add a few drops of sulphuric acid (1:1) until the *p*H of the solution is between 3 and 5.

> NOTE — Very small amounts of solution should be withdrawn in the *p*H test measurements to ensure that significant amounts of vanadium are not lost. This is conveniently done by wetting the *p*H test paper with a very small amount of solution on the end of a stirring rod which has been drawn out to about 1 mm in diameter.

9.8 An intense yellow colour in the sample solution indicates that too much vanadium is present for satisfactory photometric measurement. In this case, dilute the solution to volume in a 50-ml volumetric flask with water. Pipette an appropriate aliquot into a 100-ml borosilicate glass beaker and continue as described in **9.9**.

9.9 Add to the beaker by means of a pipette, in the order listed: 2 ml of sulphuric acid (1:1), 5 ml of phosphoric acid (1:2), and 2·5 ml of sodium tungstate solution. Heat the solution to near boiling, cool to room temperature and quantitatively transfer into a 50-ml volumetric flask. Dilute to volume with water and allow to stand for one hour.

> NOTE — Correct amounts of colour-developing reagents are given for a final sample dilution of 50 ml. Use only half of the amounts for a final dilution of 25 ml.

9.10 Carefully examine the solution for turbidity, and if present, centrifuge until clear. Transfer a portion of the clear solution into an absorption cell and measure the absorbance or transmittance of the coloured solution against the reagent blank at 436 nm.

9.11 Convert the absorbance or transmittance measurement to concentration of vanadium in milligrams of vanadium per 50 ml by means of the calibration curve (*see* **8**).

10 CALCULATION AND REPORTING

10.1 Calculate the vanadium content of the sample, in parts per million as follows:

$$\text{Vanadium, ppm} = \frac{C \times 1\,000}{M}$$

where

C = vanadium concentration, in milligrams per 50 ml, corresponding to the measured absorbance or transmittance; and

M = mass in g of the sample used.

NOTE — If an aliquot was taken in **9.8**, multiply the value calculated from the equation by $50/A$, where A equals the size of the aliquot in millilitres.

10.2 Report the result as vanadium content in ppm.

11 PRECISION

Results of duplicate tests shall not differ by more than the following amounts:

Range, ppm	*Repeatability*, ppm	*Reproductivity*, ppm
0 to 2	0·3 ppm of vanadium	—
2 to 350	10 percent of vanadium content	—
0 to 6	—	50 percent of vanadium content
6 to 350	—	17 percent of vanadium content

ANNEX A

(*Clause* 6)

PRECAUTIONARY STATEMENTS

A-1 NITRIC ACID (CONCENTRATED)

Danger — Poison. Corrosive. Strong oxidizer. Contact with organic material may cause fire. May be fatal if swallowed. Liquid and vapour cause severe burns. Harmful if inhaled. May cause delayed lung injury. Spillage may cause fire or liberate dangerous gas, or both.

Do not get in eyes, on skin, or on clothing.
Do not breathe vapour, spray, or mist.
Dilute by adding acid to water.
Keep in tightly closed container in approved acid storage cabinet.
Keep cool.
Loosen closure carefully when opening.
Use with adequate ventilation.
Keep from contact with combustible materials including clothing.
Do not store near combustible materials.
Keep container closed when not in use.
Use protective clothing and goggles when handling.
Wash thoroughly after handling.

A-2 PHOSPHORIC ACID (CONCENTRATED)

Danger — Poison. Corrosive. May be fatal if swallowed. Causes severe burns. Harmful if inhaled.

Do not get in eyes, on skin, or on clothing.
Do not breathe vapour, spray, or mist.
Dilute by addition of acid to water.
Keep in tightly closed container in approved acid storage cabinet.
Keep cool.
Loosen closure carefully when opening.
Use with adequate ventilation.
Keep container closed when not in use.
Use protective clothing and goggles when handling.
Wash thoroughly after handling.

A-3 POTASSIUM PERMANGANATE

Danger — Ingestion may cause nausea, vomiting, renal damage. Decomposes with explosive violence under certain conditions of excessive heat. Hazardous with sulphuric acid and organics.

A-4 SODIUM HYDROXIDE

Danger — Corrosive. Can cause severe burns or blindness. Evolution of heat produces a violent reaction or eruption upon too rapid mixtures with water.

Before using, secure information on procedures and protective measures for safe handling.

Do not get in eyes, on skin, or clothing.
Avoid breathing dusts or mists.
Do not take internally.

When handling, use chemical safety goggles or face shield, protective gloves, boots, and clothing.

When mixing with water, add slowly to surface of solution to avoid violent spattering. In the preparation of solutions do not use hot water, limit temperature rise with agitation, to 10°C/min or limit solution temperature to a maximum of 90°C. No single addition should cause a concentration increase greater than 5 percent.

A-5 SULPHURIC ACID (CONCENTRATED)

Danger — Poison. Corrosive. Strong oxidizer. Contact with organic material may cause fire. May be fatal if swallowed. Liquid and vapour cause severe burns. Harmful if inhaled. Contact with water liberates large amounts of heat. Spillage may cause fire.

Do not get in eyes, on skin, or on clothing.

Do not breathe vapour, spray, or mist.

Dilute by addition of acid to water.

Keep in tightly closed container in approved acid storage cabinet.

Keep cool.

Loosen closure carefully when opening.

Use with adequate ventilation.

Do not allow water to get into container because of violent reaction.

Keep container closed when not in use.

Use protective clothing and goggles when handling.

Wash thoroughly after handling.

A-6 VANADIUM PENTOXIDE

Danger — Poison. May be fatal if inhaled. Harmful if swallowed or absorbed through skin. Causes eye and internal irritation. Do not breathe dust or fumes. Use only with adequate ventilation.

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